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1. I am a citizen of Japan residing at 5-1-615, Higashiikebukuro 4-chome, Toshima-ku, Tokyo, Japan.
2. To the best of my ability, I translated:

Japanese Patent Application No. 2003-021009

from Japanese into English and the attached document is a true and accurate English translation thereof.

2. I further declare that all statements made herein are true, and that all statements made on information and belief are believed to be true; and further that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Date: January 25, 2008



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Kenji Takaishi

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**Attached Papers**

Specification One  
Abstract One  
General Power of Attorney No. 9907443

**Necessity for Proof** Yes

## SPECIFICATION

### Title of the Invention

PRINTED CIRCUIT BOARD, METHOD FOR PRODUCING SAME,  
5 AND INK THEREFOR

### CLAIMS:

1. A printed circuit board comprising a conductive pattern formed by applying a dispersion comprising fine particles of a metal oxide or  
10 hydroxide onto a support, and reducing at least part of said fine metal oxide or hydroxide particles by energy irradiation to a metal.
2. A printed circuit board of claim 1, wherein said dispersion further comprises a reducing agent that has substantially no reducing activity to said fine particles of a metal oxide or hydroxide at room  
15 temperature but can exhibit said reducing activity by energy irradiation.
3. A printed circuit board comprising a conductive pattern formed by separately preparing a dispersion of fine particles of a metal oxide or hydroxide, and a reducing agent having a reducing activity to said  
20 fine particles of a metal oxide or hydroxide or its solution; mixing the both liquids immediately before use and applying the mixed liquid onto a support, or applying the both liquids separately onto the support such that they are mixed with each other on the support; and then reducing at least part of the fine metal oxide or hydroxide particles by  
25 energy irradiation to a metal.
4. A printed circuit board of claim 1 or 2, wherein the dispersion comprising fine metal oxide or hydroxide particles comprises a base or a base precursor.
5. A printed circuit board of claim 3, wherein the dispersion

comprising fine metal oxide or hydroxide particles or another liquid (a reducing agent or its solution) comprises a base or a base precursor.

6. A printed circuit board of any one of claims 1 to 5, wherein a metal constituting said fine particles of a metal oxide or hydroxide is at least one selected from the group consisting of Au, Ag, Cu, Pt, Pd, In, Ga, Sn, Ge, Sb, Pb, Zn, Bi, Fe, Ni and Co.

7. A printed circuit board of claim 6, wherein a metal constituting said fine particles of a metal oxide or hydroxide is Ag or Cu.

8. A printed circuit board of any one of claims 1, 2, 4, 6 and 7, wherein said energy irradiation is achieved using at least one selected from the group consisting of laser beams, electron beams, ion beams or heat rays.

9. A printed circuit board of any one of claims 2 to 8, wherein said reducing agent is at least one compound selected from the group consisting of organic reducing agents, hydrazine and hydroxylamine.

10. A printed circuit board of claim 9, wherein said organic reducing agent is at least one organic compound selected from the group consisting of hydrazine derivatives, hydroxylamine derivatives, diols, and compounds represented by the general formula of  $X-(A=B)_n-Y$ , wherein each of A and B represents a carbon or nitrogen atom, each of X and Y represents an atomic group having an atom with a lone electron pair bonded to A or B, and  $n$  represents 0 to 3.

11. A method for producing a printed circuit board comprising the steps of applying a dispersion comprising fine particles of a metal oxide or hydroxide onto a support, and reducing at least part of said fine metal oxide or hydroxide particles by energy irradiation to a metal, thereby forming a conductive pattern.

12. A method of claim 11, wherein a reducing agent that has

substantially no reducing activity to said fine particles of a metal oxide or hydroxide at room temperature but can exhibit said reducing activity by energy irradiation is added to said dispersion.

13. A method of claim 11 or 12, wherein a base or a base precursor  
5 is added to a dispersion comprising fine metal oxide or hydroxide particles.

14. A method of any one of claims 11 to 13, wherein said  
conductive pattern is formed by inputting pattern information into a  
computer, and ejecting said printed circuit board-producing ink  
10 according to the pattern information.

15. A method of any one of claims 11 to 13, wherein said  
conductive pattern is formed by coating said dispersion onto a support,  
and then energy-irradiating onto the coated surface according to the  
pattern information.

16. A method for producing a printed circuit board comprising the  
steps of (a) separately preparing a dispersion of fine particles of a  
metal oxide or hydroxide, and a reducing agent having a reducing  
activity to the fine particles of a metal oxide or hydroxide or its  
solution; (b) mixing the both liquids immediately before use and  
20 applying the mixed liquid onto a support, or applying the both liquids  
separately onto the support such that they are mixed with each other  
on the support; and then (c) reducing at least part of the fine metal  
oxide or hydroxide particles by energy irradiation to a metal.

17. A method of claim 16, wherein a base or a base precursor is  
25 added to a dispersion comprising fine metal oxide or hydroxide  
particles or another liquid (a reducing agent or its solution).

18. A method of claim 16 or 17, wherein said dispersion, said  
reducing agent or its solution, or mixed liquid thereof is ejected onto a

support according to graphic information of a conductive pattern input into a computer.

19. A method of claim 16 or 17, wherein a conductive pattern is formed by coating said dispersion, said reducing agent or its solution, or mixed liquid thereof onto a support, and then energy-irradiating onto the coated surface according to graphic information of said conductive pattern input into a computer.

20. A method of any one of claims 11 to 15 and 19, wherein said energy irradiation is achieved using at least one selected from the group consisting of laser beams, electron beams, ion beams or heat rays.

21. A method of any one of claims 11 to 20, wherein a metal constituting said fine particles of a metal oxide or hydroxide is at least one selected from the group consisting of Au, Ag, Cu, Pt, Pd, In, Ga, Sn, Ge, Sb, Pb, Zn, Bi, Fe, Ni and Co.

22. A method of claim 21, wherein a metal constituting said fine particles of a metal oxide or hydroxide is Ag or Cu.

23. A method of any one of claims 11 to 22, wherein said reducing agent is at least one compound selected from the group consisting of organic reducing agents, hydrazine and hydroxylamine.

24. A method of claim 23, wherein said organic reducing agent is at least one organic compound selected from the group consisting of hydrazine derivatives, hydroxylamine derivatives, diols, and compounds represented by the general formula of X-

(A=B)<sub>n</sub>-Y, wherein each of A and B represents a carbon or nitrogen atom, each of X and Y represents an atomic group having an atom with a lone electron pair bonded to A or B, and *n* represents 0 to 3.

25. A printed circuit board-producing ink comprising at least a

dispersion comprising fine particles of a metal oxide or hydroxide.

26. A printed circuit board-producing ink comprising at least 2 parts of a dispersion comprising fine metal oxide or hydroxide particles and another liquid (a reducing agent or its solution).

- 5 27. A printed circuit board-producing ink comprising at least 2 parts of a dispersion comprising fine metal oxide or hydroxide particles and a solution comprising a base or a base precursor.

DETAILED DESCRIPTION OF THE INVENTION

【0001】

Field of the Invention

- The present invention relates to a printed circuit board, and
- 5 particularly to a printed circuit board having a circuit formed by an on-demand method, a method capable of producing a printed circuit board having a dense circuit with ease, and an ink therefor.

【0002】

Prior Art

- 10 Known as methods for forming a conductive pattern on a support are (i) methods in which a conductive film of silver, copper, etc. is formed over a support by sputtering, vacuum deposition, electroless plating, bonding a metallic foil, etc. and etched into a desired pattern by photolithography; (ii) methods in which a mask is
- 15 used in electroless plating, vacuum deposition, etc. to form a conductive pattern; (iii) methods in which a pattern is drawn with a solder or a conductive paste on a support; (iv) methods in which an anisotropic conductive film is formed and attached in a desired pattern under pressure; etc. However, it is difficult to rapidly form a dense
- 20 conductive pattern by these methods.

【0003】

- In addition to the above methods, also known are methods in which a silver ink is discharged by an ink-jet apparatus, a dispenser, etc. to form a conductive pattern of silver, described in JP 2002-
- 25 299833 A (Patent Document 1), etc. However, when the metal particles has a size of several tens nm or less, the conductive pattern has a large surface area and thus can be easily oxidized to show considerably increased resistance value. This phenomenon is notably



seen in the case of using nanoparticles of a metal such as copper and tin with a lower standard electrode potential. Thus, the methods are disadvantageous in that it is difficult to store and handle the ink.

Further, disclosed in JP 59-36993 A (Patent Document 2) is a method  
5 in which an insulating material such as  $\text{Cu}_2\text{O}$ , a mixture of  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$ , and a mixture of  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$  is formed into a film by a gas phase method such as sputtering, ion plating and CVD, and the film is partly converted into a metal by selective energy irradiation to form a conductive pattern. This method can form the conductive pattern  
10 with a flat surface, thereby suitable for forming a multilayer circuit structure. However, the method has disadvantages of requiring more time for the film formation and unsuitability for on-demand processes.

【0004】

[Patent Document 1]

15 JP 2002-299833 A

[Patent Document 2]

JP 59-36993 A

【0005】

Problems to be Solved by the Invention

20 Accordingly, an object of the present invention is to provide an on-demand printed circuit board that can have a multilayer circuit structure.

【0006】

Another object of the present invention is to provide a method  
25 for producing a multilayer printed circuit board, which can form a dense conductive pattern easily and rapidly.

【0007】

A further object of the present invention is to provide an ink

for producing a multilayer printed circuit board, which can form a dense conductive pattern easily and rapidly.

【0008】

Means for Solving the Problems

5           A first printed circuit board of the present invention comprises a conductive pattern, which is formed by applying a dispersion comprising fine particles of a metal oxide or hydroxide onto a support, and reducing at least part of the fine metal oxide or hydroxide particles by energy irradiation to a metal.

10       【0009】

          A second printed circuit board of the present invention comprises a conductive pattern, wherein the conductive pattern is formed by applying a dispersion comprising fine particles of a metal oxide or hydroxide, and a reducing agent that has substantially no  
15   reducing activity to the fine particles of a metal oxide or hydroxide at room temperature but can exhibit the reducing activity by energy irradiation onto a support, and reducing at least part of the fine metal oxide or hydroxide particles by energy irradiation to a metal.

【0010】

20           A third printed circuit board of the present invention comprises a conductive pattern, wherein the conductive pattern is formed by separately preparing a dispersion of fine particles of a metal oxide or hydroxide, and a reducing agent having a reducing activity to the fine particles of a metal oxide or hydroxide or its solution; mixing the both  
25   liquids immediately before use and applying the mixed liquid onto a support, or applying the both liquids separately onto the support such that they are mixed with each other on the support; and then reducing at least part of the fine metal oxide or hydroxide particles by energy

irradiation to a metal.

**[0011]**

A first method of the present invention for producing a printed circuit board comprises the steps of applying a dispersion comprising  
5 fine particles of a metal oxide or hydroxide onto a support, and reducing at least part of the fine metal oxide or hydroxide particles by energy irradiation to a metal, thereby forming a conductive pattern.

**[0012]**

A second method of the present invention for producing a  
10 printed circuit board comprises the steps of applying a dispersion comprising fine particles of a metal oxide or hydroxide, and a reducing agent that has substantially no reducing activity to the fine particles of a metal oxide or hydroxide at room temperature but can exhibit the reducing activity by energy irradiation onto a support, and reducing at  
15 least part of the fine metal oxide or hydroxide particles by energy irradiation to a metal, thereby forming a conductive pattern.

**[0013]**

A third method of the present invention for producing a printed circuit board comprises the steps of (a) separately preparing a  
20 dispersion of fine particles of a metal oxide or hydroxide, and a reducing agent having a reducing activity to the fine particles of a metal oxide or hydroxide or its solution; (b) mixing the both liquids immediately before use and applying the mixed liquid onto a support, or applying the both liquids separately onto the support such that they  
25 are mixed with each other on the support; and then (c) reducing at least part of the fine metal oxide or hydroxide particles by energy irradiation to a metal.

**[0014]**

The printed circuit boards and the methods of the present invention preferably meet following conditions.

- (1) The dispersion comprising fine metal oxide or hydroxide particles or another liquid (a reducing agent or its solution) comprises  
5 a base or a base precursor.
- (2) The metal oxide or hydroxide comprises at least one metal selected from the group consisting of Au, Ag, Cu, Pt, Pd, In, Ga, Sn, Ge, Sb, Pb, Zn, Bi, Fe, Ni and Co.
- (3) The metal oxide or hydroxide comprises Ag or Cu.
- 10 (4) The reducing agent comprises at least one compound selected from the group consisting of organic reducing agents, hydrazine, and hydroxylamine.
- (5) The organic reducing agent is an organic compound selected from the group consisting of hydrazine-based compounds,  
15 hydroxylamine-based compounds, diol compounds, and compounds represented by the general formula  $X-(A=B)_n-Y$ , in which A and B represent a carbon atom or a nitrogen atom respectively, X and Y represent an atomic group having an atom with a lone electron pair bonding to A or B respectively, and n represents 0 to 3.
- 20 (6) The energy irradiation is achieved using at least one selected from the group consisting of a laser beam, an electron beam, an ion beam, or a heat ray.

【0015】

The printed circuit boards and the methods of the present invention preferably meet further following conditions.

- (7) The conductive pattern is formed by inputting pattern information into a computer, and then ejecting an ink onto a support according to the pattern information.

(8) The conductive pattern is formed by coating an ink onto a support, and then energy-irradiating onto the coated surface according to pattern information input into a computer.

【0016】

5 A printed circuit board-producing ink of the present invention comprises a dispersion at least comprising fine particles of a metal oxide or hydroxide; 2 parts of a dispersion comprising fine particles of a metal oxide or hydroxide and a solution containing a reducing agent; or 2 parts of a dispersion comprising fine particles of a metal oxide or  
10 hydroxide and a solution comprising a base or a base precursor.

【0017】

When the board, onto which the printed circuit board-producing ink of the present invention is applied, is irradiated with energy, fine particles of the metal oxide or hydroxide are at least partly  
15 reduced to form a conductive pattern composed of a metal. Even a mild reducing agent, which is stable and hardly reduces the metal oxide or hydroxide at ordinary temperature, is preferably combined, because the agent can exhibit reducing activity by energy irradiation. The insulating layer of the fine metal oxide particles is converted into  
20 a conductive layer having a pattern by selectively reducing the metal oxide or hydroxide with narrowing the energy beam down. Thus, the conductive pattern can be formed in a flat surface, so that a multilayer circuit pattern can be obtained. In addition, when the ink is ejected by the means such as an inkjet, a dispenser, etc., the pattern with high  
25 density can be easily and rapidly obtained on demand. In this case, the energy irradiation may be conducted onto overall or a part of ejected area.

【0018】

## Mode for Carrying Out the Invention

The present invention will be described in detail below.

[1] Dispersion liquid of fine particles of metal oxide or hydroxide

(A) Composition and size of fine particles of metal oxide or

5 hydroxide

The fine particles of the metal oxide or hydroxide used in the present invention may comprise a metal atom such as Au, Ag, Cu, Pt, Pd, In, Ga, Sn, Ge, Sb, Pb, Zn, Bi, Fe, Ni, Co, Mn, Ti, Cr, V, Ru, Rh, Ir, and Al. The metal oxide or hydroxide is preferably an oxide of

10 Au, Ag, Cu, Pt, Pd, In, Ga, Sn, Ge, Sb, Pb, Zn, Bi, Fe, Ni, or Co.

Oxides of Ag or Cu such as  $\text{Ag}_2\text{O}$  and  $\text{Cu}_2\text{O}$  are particularly preferred as the metal oxide or hydroxide because they can be easily reduced to generate a relatively stable metal. The average crystallite size of the fine particles is 1 to 100 nm, preferably 1 to 50 nm.

15 【0019】

(B) Preparation method

The dispersion liquid of the fine particles of the metal oxide or

hydroxide may be prepared by neutralizing a solution of a metal salt such as a chloride, a bromide, a sulfate, a nitrate or an organic salt of

20 the above metal with a basic solution; or by hydrolyzing a metal alkoxide; or by adding a reducing agent to a solution of a high-valent metal salt to reduce the salt into a low-valent metal oxide or hydroxide; etc. Examples of organic acids of the organic salts

25 isobutyric acid, 2-ethylbutyric acid, pivalic acid, valeric acid, isovaleric acid, propiolic acid, lactic acid, caproic acid, caprylic acid, capric acid, benzoic acid, phthalic acid, salicylic acid, acrylic acid, methacrylic acid, ethylmethylacetic acid, allylacetic acid, and

acetoacetic acid.

【0020】

- The fine particles of the metal oxide or hydroxide are preferably surface-modified by adsorbing an adsorbent compound, a  
5 surfactant and/or a hydrophilic polymer to the fine particles, to stabilize the dispersion liquid if necessary.

【0021】

- The dispersion liquid may be subjected to centrifugal separation, etc. to precipitate the fine particles of the metal oxide or  
10 hydroxide in the presence of the adsorbent compound and/or the surfactant, and the obtained fine particles may be washed and redispersed in another dispersion solvent, if necessary. Further, the dispersion liquid may be subjected to a purification or concentration treatment such as desalination.

15 【0022】

(a) Adsorbent compound

- Compounds having a functional group such as -SH, -CN, -NH<sub>2</sub>, -SO<sub>2</sub>OH, -SOOH, -OPO(OH)<sub>2</sub> and -COOH are useful as the adsorbent compound. Particularly, preferred adsorbent compounds  
20 include compounds having -SH such as dodecanthiol and L-cysteine, and compounds having -NH<sub>2</sub> such as octylamine, dodecylamine, oleylamine, oleic amide, and lauric amide. In the case of using a hydrophilic colloid, the adsorbent compound preferably has a hydrophilic group such as -SO<sub>3</sub>M and -COOM, in which M represents  
25 a hydrogen atom, an alkaline metal atom, or an ammonium group.

【0023】

(b) Surfactant

The surfactant may be an anionic surfactant such as sodium

bis(2-ethylhexyl)sulfosuccinate and sodium dodecylbenzenesulfonate; a nonionic surfactant such as an alkyl ester and an alkyl phenyl ether of a polyalkyl glycol; or a fluorine-based surfactant; etc.

【0024】

5 (c) Hydrophilic polymer

Polymers such as hydroxyethyl cellulose, polyvinylpyrrolidone, polyvinyl alcohol, and polyethylene glycol may be contained in the colloidal dispersion liquid as the hydrophilic polymer.

10 【0025】

(d) Amount

The amount of the adsorbent compound, the surfactant and/or the hydrophilic polymer is preferably 0.01 to 2 parts by mass, more preferably 0.1 to 1 part by mass, per 1 part of the fine particles of the  
15 metal oxide or hydroxide. The fine particles are preferably covered with the coating of the adsorbent compound, the surfactant and/or the hydrophilic polymer having a thickness of 0.1 to 10 nm. The coating may be nonuniform and may cover only a small portion of the fine particles.

20 【0026】

It can be confirmed that the fine particles are surface-modified with an organic compound such as the adsorbent compound, the surfactant, and the hydrophilic polymer by observing regularity of distance between the fine particles using a high-resolution TEM such  
25 as an FE-TEM or by a chemical analysis.

【0027】

(e) Solvent

Examples of solvents for the dispersion liquid of the metal



- oxide or hydroxide (or solvents for the ink to be hereinafter described) include (1) esters such as butyl acetate and cellosolve acetate; (2) ketones such as methyl ethyl ketone, cyclohexanone, methyl isobutyl ketone, and acetylacetone; (3) chlorinated hydrocarbons such as
- 5 dichloromethane, 1,2-dichloroethane, and chloroform; (4) amides such as dimethylformamide; (5) aliphatic hydrocarbons such as cyclohexane, heptane, octane, isooctane, and decane; (6) aromatic hydrocarbons such as toluene and xylene; (7) ethers such as tetrahydrofuran, ethyl ether, and dioxane; (8) alcohols such as ethanol,
- 10 n-propanol, isopropanol, n-butanol, diacetone alcohol, ethylene glycol, 2,5-hexanediol, 1,4-butanediol, cyclohexanol, cyclopentanol, and cyclohexenol; (9) fluorine-containing solvents such as 2,2,3,3-tetrafluoropropanol; (10) glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and propylene
- 15 glycol monomethyl ether; (11) alkylaminoalcohols such as 2-dimethylaminoethanol, 2-diethylaminoethanol, 2-dimethylaminoisopropanol, 3-diethylamino-1-propanol, 2-dimethylamino-2-methyl-1-propanol, 2-methylaminoethanol, and 4-dimethylamino-1-butanol; (12) carboxylic acids such as butyric acid,
- 20 isobutyric acid, 2-ethylbutyric acid, pivalic acid, valeric acid, propionic acid, lactic acid, acrylic acid, methacrylic acid, propiolic acid, ethylmethylacetic acid, and allylacetic acid; (13) amines such as diethylenetriamine and ethylenediamine; and (14) water.

【0028】

- 25 These solvents may be used alone or in combination depending on the dispersion stability of a metal oxide or hydroxide, the solubility of a reducing agent, the oxidation stability of the reducing agent, the viscosity, etc. The solvent (common solvent) is preferably selected

such that the metal oxide or hydroxide shows excellent dispersibility and the reducing agent shows excellent solubility.

【0029】

(C) Dispersion liquid

- 5           The ratio of metals contained in the fine particles of the metal oxide or hydroxide to the dispersion liquid is preferably 1 to 80% by mass, more preferably 5 to 70% by mass. In the dispersion liquid, the fine particles may be composed of one kind or a plurality of kinds of the fine particles of the metal oxide or hydroxide. Further, the
- 10   metals in the fine particles may have the same or different valences. Inorganic fine particles of SiO, SiO<sub>2</sub>, TiO<sub>2</sub>, etc. or a polymer, which may or may not be in a state of fine particles, may be used with the fine particles of the metal oxide or hydroxide to control insulativity and conductivity of the energy-irradiated portions and unirradiated
- 15   portions. The particle diameter of the fine particles of the metal oxide or hydroxide in the dispersion liquid is not restrictive and generally such that the fine particles form colloid. The particle diameter is preferably 1 to 100 nm, more preferably 1 to 50 nm.

【0030】

20   [2] Ink

- The above-described dispersion liquid comprising the fine particles of the metal oxide or hydroxide may be used as ink without modification. A reducing agent may be added to the dispersion liquid when it is difficult to reduce the metal oxide or hydroxide by the
- 25   energy irradiation.

【0031】

          The reducing agent for reducing the metal oxide or hydroxide may be an inorganic reducing agent or an organic reducing agent.

Examples of the inorganic reducing agents include  $\text{NaBH}_4$ , hydrazine, hydroxylamine, etc. Examples of the organic reducing agents include (i) hydrazine-based compounds having a hydrazine group such as phenylhydrazine; (ii) amines such as *p*-phenylenediamine, ethylenediamine, alkylaminoalcohol and *p*-aminophenol; (iii) diols such as hydroquinone, catechol, 1,4-butanediol, and ethylene glycol; (iv) compounds represented by the general formula  $\text{X}-(\text{A}=\text{B})_n-\text{Y}$ , in which A and B represent a carbon atom or a nitrogen atom respectively, X and Y represent an atomic group having an atom with a lone electron pair bonding to A or B respectively, and n represents 0 to 3; tautomers thereof; compounds which can be thermally converted thereto; etc.

**[0032]**

These reducing agents can reduce the metal oxide or hydroxide selectively, whereby these reducing agents may be appropriately selected depending on the selectivity. These reducing agents may be used alone or combined. The reducing agents may be used in state of an organic solution if necessary.

**[0033]**

In the compounds represented by the general formula  $\text{X}-(\text{A}=\text{B})_n-\text{Y}$  of (iv), the atom with a lone electron pair is preferably an oxygen atom, a nitrogen atom, a sulfur atom, or a phosphorus atom, more preferably an oxygen atom or a nitrogen atom. The atomic groups of X and Y having such atoms are preferably  $\text{OR}_1$ ,  $\text{NR}_1\text{R}_2$ ,  $\text{SR}_1$ , or  $\text{PR}_1\text{R}_2$ , respectively, in which  $\text{R}_1$  and  $\text{R}_2$  each represent a hydrogen atom or a substituent. The substituent is preferably an alkyl or acyl group with 1 to 10 carbon atom, which may further have a substituent.

**[0034]**

n is preferably 0 to 3, more preferably 0 to 2, most preferably 0 to 1. When n is 2 or more, A's and B's in the repeating units may be different atoms. A and B, X and A, and Y and B may bond together to form a ring structure, respectively. The ring structure preferably  
5 comprises a 5- or 6-membered ring, which may form a condensed ring with another ring. The other ring is preferably a 5- or 6-membered ring.

【0035】

In the invention, the reducing agent preferably shows a low  
10 electric conductivity after the reduction reaction. Specifically, the reducing agent is preferably such that no metal ions remain in the conductive pattern after the reduction reaction, such as the organic reducing agents, hydrazine, and hydroxylamine. Because the residue of the reducing agent can have negative effects on the conductivity of  
15 the printed circuit after the reduction reaction, the residue is preferably smaller in amount. Thus, the reducing agent is preferably such that the residue is volatile (or sublime) or decomposed to be volatile after the reduction reaction.

【0036】

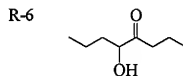
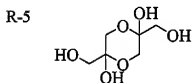
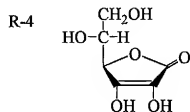
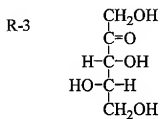
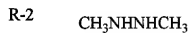
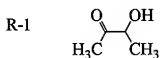
20 It is preferred that a small amount of the reducing agent can reduce the metal oxide or hydroxide from this viewpoint, and thus the reducing agent preferably has a low molecular weight. The molecular weight of the reducing agent is preferably 500 or less, more preferably 300 or less, most preferably 200 or less.

25 【0037】

Specific examples of the reducing agents used in the invention for reducing the metal oxide or hydroxide will be illustrated below without intention of restricting the scope of the invention.

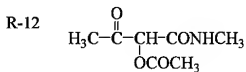
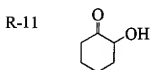
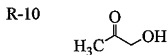
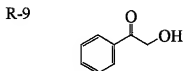
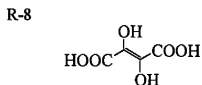
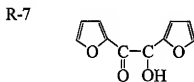
【0038】

[Chemical Formula 1]



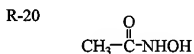
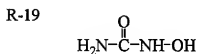
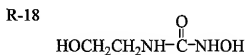
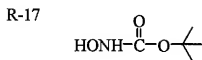
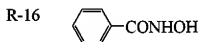
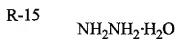
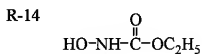
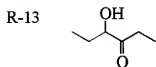
【0039】

5 [Chemical Formula 2]



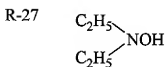
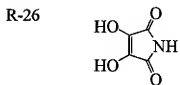
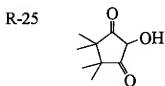
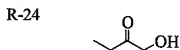
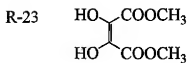
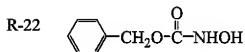
【0040】

[Chemical Formula 3]



【0041】

[Chemical Formula 4]



【0042】

The fine particles of the metal oxide or hydroxide and the reducing agent are preferably used in combination as (a) a one-component ink composed of one dispersion liquid comprising the fine particles and the reducing agent, wherein the reducing agent is capable of reducing the metal oxide or hydroxide under the energy irradiation though it is substantially incapable of reducing the metal oxide or hydroxide at ordinary temperature; or (b) two-component ink composed of the dispersion liquid comprising the fine particles and a liquid comprising the reducing agent capable of reducing the metal oxide or hydroxide, the liquids being separately prepared, wherein the dispersion liquid may be free of reducing agents, and the reducing agent has high reducing ability at least under the energy irradiation though it may have any reducing ability at ordinary temperature.

15   【0043】

In the case where the reduction reaction between the metal oxide or hydroxide and the reducing agent hardly proceeds under the energy irradiation, or in the case where higher reducing ability is required under the energy irradiation, a reduction promoter such as a base and a base precursor may be added to the dispersion liquid of the metal oxide or hydroxide or the liquid of the reducing agent. The base and the base precursor may have reducing ability.

20   【0044】

As described above, it is preferred that the reducing agent used in the invention shows a low reduction rate at ordinary temperature and can rapidly reduce the metal oxide or hydroxide under the energy irradiation. The heating temperature by thermal diffusion is preferably about 300 °C or less, more preferably about 250 °C or less,

because of heat resistance of the board and device. Thus, it is preferred that the reducing agent can sufficiently reduce the metal oxide or hydroxide at approximately 300 °C or less. In the case where a reducing agent having a high reducing ability at ordinary  
5 temperature is used for the two-component ink of (b), the metal oxide or hydroxide may be reduced immediately after mixing the liquid comprising the reducing agent with the dispersion liquid comprising the fine particles, and therefore, the energy irradiation is not required necessarily.

10    **【0045】**

The dispersion liquid of the fine particles, the liquid of the reducing agent, or the mixture thereof is preferably used as ink for drawing a pattern by an ink-jet printer or a dispenser, etc. as described hereinafter, and a solvent may be added thereto to control the viscosity  
15 if necessary. The solvent for the ink may be the same as that of the dispersion liquid.

**【0046】**

Additives such as antistatic agents, antioxidants, UV absorbents, plasticizers, carbon nanoparticles, dyes, and thermosetting  
20 resins including thermosetting phenol resins may be added to the dispersion liquid of the fine particles and/or the liquid of the reducing agent depending on the purpose, if necessary.

**【0047】**

The viscosity of the ink is important in the case of using the  
25 dispersion liquid of the fine particles of the metal oxide or hydroxide, the liquid of the reducing agent, or the mixture thereof as the ink for drawing a pattern by an ink-jet printer or a dispenser. When the viscosity of the ink is too high, it is difficult to eject the ink from a



- nozzle. On the other hand, when the viscosity of the ink is too low, there is a possibility that the pattern drawn with the ink is blurred. Specifically, the viscosity of the ink is preferably 1 to 100 cP, particularly preferably 5 to 30 cP. The surface tension of the ink is
- 5 preferably 25 to 80 mN/m, particularly preferably 30 to 60 mN/m.

【0048】

### [3] Production of printed circuit board

#### (A) Support

- Examples of preferred materials for the support used in the
- 10 invention include (1) glasses such as quartz glasses, non-alkali glasses, transparent glass ceramics, pyrex glasses, and sapphire glasses; (2) ceramics such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{BeO}$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ThO}_2$ ,  $\text{CaO}$ , and GGG (gadolinium gallium garnet); (3) thermoplastic resins such as polycarbonates, acrylic resins including polymethyl methacrylates,
- 15 vinyl chloride-based resins including polyvinyl chlorides and vinyl chloride copolymers, polyarylates, polysulfones, polyethersulfones, polyimides, fluorine resins, phenoxy resins, polyolefin resins, nylons, styrene resins, and ABS resins; (4) thermosetting resins such as epoxy resins; (5) metals; etc.

20 【0049】

- The above materials for the support may be used in combination if necessary. The material for the support may be appropriately selected from these ones depending on the use, to obtain a flexible support in a shape of a film, etc. or a rigid support. The
- 25 support may have a shape of disc, card, sheet, etc. The support may have a three-dimensional laminate structure. Further, the support may have fine pores or grooves having an aspect ratio of 1 or more in portions on which the printed circuit is formed. The dispersion liquid

of the fine particles or the liquid of the reducing agent may be discharged into the fine pores or grooves by an ink-jet process or a dispenser.

【0050】

5           A ground layer may be formed on the support to improve the surface smoothness, to increase the adhesive strength, or to prevent deterioration. The ground layer is preferably composed of a material that can provide excellent adhesion between the support and the ink. Examples of such materials include (1) thermoplastic resins such as  
10   polymethyl methacrylates, acrylic acid-methacrylic acid copolymers, styrene-maleic anhydride copolymers, polyvinyl alcohols, *N*-methylolacrylamide, styrene-vinyltoluene copolymers, chlorosulfonated polyethylenes, nitrocelluloses, polyvinyl chlorides, polyvinylidene chlorides, chlorinated polyolefins, polyesters,  
15   polyimides, vinyl acetate-vinyl chloride copolymers, ethylene-vinyl acetate copolymers, polyethylenes, polypropylenes, and polycarbonates; (2) thermo-, photo-, or electron beam-hardening resins; (3) coupling agents such as silane coupling agents, titanate coupling agents, germanium coupling agents, and aluminum coupling  
20   agents; and (4) colloidal silicas; etc.

【0051】

          The ground layer may be formed by dissolving or dispersing the above material in a suitable solvent to prepare a coating liquid, and by applying the coating liquid to the support. The coating liquid may  
25   be applied by a coating method such as a spin coating method, a dip-coating method, an extrusion coating method, and a bar coating method. In general, the dry thickness of the ground layer is preferably 0.001 to 20  $\mu\text{m}$ , more preferably 0.005 to 10  $\mu\text{m}$ .

【0052】

(B) Application of ink

An ink is applied by a spin coating method, a bar coating method, a dip-coating method, an extrusion coating method, a printing method, etc. In this case, the ink may be applied on whole area or necessary portions of the support.

【0053】

In the case of drawing a pattern with the ink on the support, it is preferred that droplets of the ink are discharged from a nozzle to the support by an ink-jet printer or a dispenser. In the case of mixing the two liquids immediately before the application, the two liquids are preferably mixed by a microreactor or a micromixer.

【0054】

The microreactor and the micromixer are described in detail in Japanese Patent Application No. 2001-388572, etc. The microreactor of Japanese Patent Application No. 2001-388572 comprises a first channel for a fluid 1 and a second channel for a fluid 2, and wherein each fluid flows to form a thin layer substantially, a contact interface of the fluids is formed in at least one portion, each thin layer has a thickness of 1 to 500  $\mu\text{m}$  in the normal direction on the contact interface, and the fluids are reacted or mixed at the contact interface.

【0055】

Various types of the ink-jet printers utilizing various ink-discharging systems may be used in the invention. For example, piezoelectric element-type printers, bubble jet-type printers, air flow-type printers, thermofusionable solid ink-type printers, electrostatic induction type printers, acoustic ink-printing-type printers, electroviscous ink type printers, continuous injection type printers

suitable for mass production, etc. are known as the ink-jet printers and usable in the invention. These ink-jet printers may be selected depending on the desired shape and thickness of the pattern, the type of the ink, etc.

5      **【0056】**

The width or the pitch of the pattern can be reduced to approximately several micrometers by controlling the size of the ink droplets in the ink-jet process or by controlling the flow quantity of the ink droplets in the dispenser process. Thus, the ink-jet process  
10 and the dispenser process can be sufficiently utilized for forming the circuit pattern. The discharging portion of the ink-jet printer, the dispenser, etc. may be connected to a computer such as a personal computer to draw a pattern on the support based on pattern information input into the computer. The fine particles of the metal  
15 oxide are generally insulative, so that a pattern wider than the desired conductive pattern may be drawn with the dispersion liquid comprising the fine particles by the ink-jet printer or the dispenser, and selectively irradiated with energy to obtain a dense conductive pattern. In this case, the conductive pattern desirably has a dry  
20 thickness equal to that of the unirradiated insulative portions. The thicknesses of the conductive pattern and the insulative portions may be controlled in a range of 0.1 to 10  $\mu\text{m}$  as usage.

**【0057】**

Thus, in the invention, the conductive pattern can be formed  
25 more easily in a shorter period of time as compared with conventional methods of patterning conductive films by using photoresists.

**【0058】**

(C) Formation of conductive pattern

The energy irradiation for forming the conductive pattern may be achieved by using an electric furnace, an electromagnetic wave such as microwave, a infrared ray, a hot plate, a laser beam, an electron beam, an ion beam, or a heat ray, etc. Particularly preferred are the laser beam, the electron beam, the ion beam, and the heat ray, which can heat the applied liquid locally and minutely. The laser beam is the most preferable because it can be easily irradiated from a relatively small apparatus.

【0059】

The wavelength of the laser beam may be optionally selected from the range of the ultraviolet to infrared region as long as the fine particles of the metal oxide or hydroxide, the reducing agent, the solvent, or the carbon nanoparticles or the dye added if necessary, etc. can absorb the beam with the wavelength. Typical examples of the lasers include semiconductor lasers of AlGaAs, InGaAsP, GaN, etc.; Nd:YAG lasers; excimer lasers of ArF, KrF, XeCl, etc.; dye lasers; solid lasers such as ruby lasers; gas lasers of He-Ne, He-Xe, He-Cd, CO<sub>2</sub>, Ar, etc; and free-electron lasers. Further, surface emission type semiconductor lasers and multimode arrays comprising the lasers arranged one- or two-dimensionally may be used in the invention.

【0060】

Higher harmonics such as second harmonics and third harmonics of these laser beams may be used for the energy irradiation. The laser beams may be irradiated continuously or pulse-wise. The preferred amount of the energy depends on the type of the fine particles of the metal oxide or hydroxide, the type of the reducing agent, the type and the amount of the binder, the solvent, etc., and the amount may be such that the generated metal nanoparticles are

substantially melted without ablation by the energy irradiation.

【0061】

Among processes including mixing the liquids, forming the conductive pattern by energy-irradiating mixed liquid applied on the support, all process is preferably carried out under an inert gas. The inert gas may be nitrogen, helium, neon, argon, etc.

【0062】

The present invention will be described in more detail below with reference to Examples without intention of restricting the scope of the present invention.

【0063】

Example 1

50 g of copper (II) acetate monohydrate was dissolved in a mixed solvent of 50 ml of isobutyric acid, 70 ml of 2-ethoxyethanol, and 20 ml of water under heating at 130 °C. 1.5 ml of dodecylamine and 45 ml of the example compound R-10 were added to the resultant solution, reacted for 1 minute, and cooled to the room temperature, to obtain a reddish brown colloidal dispersion liquid. The dispersion liquid was dried and subjected to X-ray diffraction (XRD) measurement, and as a result, generation of fine Cu<sub>2</sub>O particles having the average crystallite size of 14 nm was confirmed.

【0064】

Quintuple volume of methanol was added to the obtained colloidal Cu<sub>2</sub>O dispersion liquid to precipitate Cu<sub>2</sub>O nanoparticles. The supernatant liquid was removed by decantation, and methanol was added to the residue again to wash the Cu<sub>2</sub>O nanoparticles. The processes were repeated three times, and then the Cu<sub>2</sub>O nanoparticles were redispersed in a solution of 1 ml of dodecylamine, 35 ml of 2-

ethoxyethanol, and 15 ml of water, to obtain 25% by mass dispersion liquid of the fine  $\text{Cu}_2\text{O}$  particles.

【0065】

The dispersion liquid of the fine  $\text{Cu}_2\text{O}$  particles was discharged  
5 by a dispenser onto a polyimide support along fine grooves having a depth of 50  $\mu\text{m}$  and a width of 1 mm of the support. The applied dispersion liquid had the liquid thickness of 70  $\mu\text{m}$ . Then, the dispersion liquid was dried at 80 °C by a hot plate, and irradiated with an infrared laser of 830 nm with energy of 20  $\text{J}/\text{cm}^2$ , to obtain a copper  
10 circuit having the specific resistance of 8  $\mu\Omega\cdot\text{cm}$  and the thickness of approximately 4  $\mu\text{m}$ .

【0066】

Example 2

The dispersion liquid of the fine  $\text{Cu}_2\text{O}$  particles of Example 1  
15 was spin-coated onto a flat polyimide support, and dried at 80 °C to form a  $\text{Cu}_2\text{O}$  film of thickness about 2  $\mu\text{m}$ . The  $\text{Cu}_2\text{O}$  film was irradiated with an infrared ray of energy 15  $\text{J}/\text{cm}^2$  and 830 nm according to graphic information of a conductive pattern preliminarily input into a computer, so that surface resistance was deteriorated to  
20 0.04  $\Omega/\square$  only on irradiated portions, and thus a conductive pattern was obtained.

【0067】

Example 3

The dispersion liquid of the fine  $\text{Cu}_2\text{O}$  particles and the liquid  
25 of the example compound R-10 of Example 1 were instantly mixed by a microreactor described in JP 2001-388572 A such that the volume ratio of the dispersion liquid of the fine  $\text{Cu}_2\text{O}$  particles/the liquid of the

example compound R-10 was 10/3. The resulting mixture was discharged by a dispenser onto the fine grooves of the polyimide support of Example 1. The applied mixture had the liquid thickness of 100  $\mu\text{m}$ . Then, the mixture was dried and irradiated with the  
5 infrared laser of 830 nm, to obtain a copper circuit having the specific resistance of 6  $\mu\Omega\text{-cm}$  and the thickness of approximately 4  $\mu\text{m}$ .

【0068】

#### Example 4

17 g of silver (I) nitrate was dissolved in a mixed solvent of 25  
10 ml of water and 25 ml of 2-ethoxyethanol, and cooled with ice. 500 ml of 0.1 N aqueous NaOH solution containing 50% by volume of 2-ethoxyethanol was cooled with ice and added to the resultant silver nitrate solution. Thus obtained nanoparticles were precipitated and washed in the same manner as Example 1, and redispersed in a mixed  
15 solvent of cyclohexanol and 2-ethoxyethanol (volume ratio 50:50), to obtain a 20% by mass dispersion liquid of fine  $\text{Ag}_2\text{O}$  particles. The fine  $\text{Ag}_2\text{O}$  particles had the average crystallite size of 16 nm.

【0069】

The dispersion liquid of fine  $\text{Ag}_2\text{O}$  particles was discharged by  
20 a piezo ink-jet printer at the rate of 50 picometers/droplet to draw a pattern on a polyimide support based on pattern information input into a computer preliminarily. The dispersion liquid was dried and irradiated with the infrared laser in the same manner as Example 1, whereby  $\text{Ag}_2\text{O}$  was reduced to conductive Ag.

25 【0070】

#### Effect of the Invention

As is clear from the above results, in the present invention, the conductive pattern can be easily formed by applying the dispersion



liquid comprising the fine particles of the metal oxide or hydroxide  
such as  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$  onto the support, and by reducing the metal  
oxide or hydroxide to the metal at least partly under the energy  
irradiation using a laser, etc. Thus, the printed circuit boards can be  
5 rapidly and stably produced with ease by the methods of the invention.

## Abstract

### Problems to be solved:

An on-demand printed circuit board that can have a multilayer  
5 circuit structure, and a production method thereof, are provided.

### Solution:

A method for producing a printed circuit board comprising the steps  
of applying a dispersion comprising fine particles of a metal oxide or  
hydroxide onto a support, and reducing at least part of said fine metal oxide  
10 or hydroxide particles by energy irradiation to a metal, thereby forming a  
conductive pattern.

**Selected Drawings:** None